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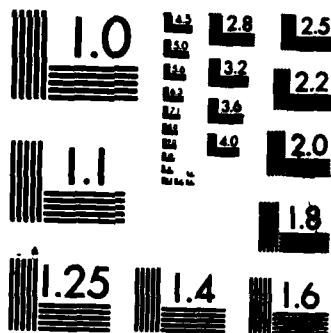UNCLASSIFIED   N00014-82-K-0612   F/G 11/9   NL

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Electronically Conductive Composite Polymer Membranes

by

Reginald M. Penner and Charles R. Martin

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We have recently described the preparation and properties of ionically conductive Nafion-impregnated Gore-tex (NIGT) composite membranes (reference 10). In this paper we describe electronically conductive composite membranes prepared by electropolymerizing either pyrrole or thiophene within the ionically conductive NIGT membrane. These composites have the mechanical properties of the host membrane yet the electronic conductivity of the NIGT/polypyrrole composite membrane is essentially identical to that of polypyrrole. (con

20.   Abstract

For comparison, we have also attempted to electropolymerize pyrrole in Nafion membranes and films and in bare Gore-tex and poly(vinyl chloride)-impregnated Gore-tex. We have found that the rate of polymerization of pyrrole at a NIGT-coated Pt electrode is higher than the rate at bare Pt. The origins of this rate enhancement are probed.

Electronically Conductive Composite Polymer Membranes

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ABSTRACT

We have recently described the preparation and properties of ionically conductive Nafion-impregnated Gore-tex (NIGT) composite membranes (reference 10). In this paper we describe electronically conductive composite membranes prepared by electropolymerizing either pyrrole or thiophene within the ionically conductive NIGT membrane. These composites have the mechanical properties of the host membrane yet the electronic conductivity of the NIGT/polypyrrole composite membrane is essentially identical to that of polypyrrole. For comparison, we have also attempted to electropolymerize pyrrole in Nafion membranes and films and in bare Gore-tex and poly(vinyl chloride)-impregnated Gore-tex. We have found that the rate of polymerization of pyrrole at a NIGT-coated Pt electrode is higher than the rate at bare Pt. The origins of this rate enhancement are probed.

A considerable amount of research effort is currently being devoted to studies of electronically conductive polymers (1-4). While a number of systems have been investigated, polymers based on heterocyclic monomers (e.g., pyrrole) offer a number of important advantages (2-4). These polymers are more stable than, for example polyacetylene, they can be very conductive, and they can be conveniently synthesized via electropolymerization (2-4). On the other hand, polypyrrole and its analogs are hard and brittle materials; these undesirable mechanical characteristics severely restrict the technological applications of these polymers (5).

Diaz et al. have recently prepared poly(vinyl chloride)-polypyrrole composite membranes by electropolymerizing pyrrole inside a poly(vinyl chloride) (PVC) film on an electrode surface (6,7). These composites had the desirable mechanical properties of the PVC host yet retained the high conductivity of the polypyrrole (PP) dopant (6,7). Because it is inherently neither porous nor ionically conductive, PVC is not the ideal host material for the preparation of conductive composites. This is evidenced by the long polymerization times required for the preparation of thin (less than 10 μm) PVC/PP composite films (6). The ideal host material would be mechanically stable, chemically inert, porous (to allow for impregnation by PP), and ionically conductive (to allow for quick ingress and egress of charge compensating ions). Furthermore, it would be advantageous for the host material to be a free standing membrane (rather than a film cast on the electrode surface) so that the conductive composite could be easily removed, intact, from the electrode after doping.

We have recently prepared ionically conductive composite membranes by doping a host polytetrafluoroethylene membrane, Gore-tex (8), with a perfluorosulfonate ionomer, du Pont's Nafion (9), (10). Gore-tex (GT) is mechanically and chemically stable and has an open, porous stucture. Because it is hydrophobic, GT is not wetted by water and, therefore, not ionically conductive when contacted with an aqueous electrolyte phase (10). We have shown, however, that when GT is

impregnated with Nafion, the resulting composite is water wetted and is an ionic conductor. Because GT has an open, porous structure, Nafion-impregnated Gore-tex (NIGT) is a better ionic conductor than Nafion itself (10).

The above discussion suggests that NIGT would be an ideal host material for the preparation of electronically conductive composite membranes. We have electropolymerized pyrrole and thiophene in NIGT and have examined the conductivities and electrochemical characteristics of the resulting composite membranes. For comparison, we have also attempted to grow PP in GT which does not contain Nafion, in Nafion (both as-received membrane and solution-cast film), and in PVC-impregnated GT (PVCIGT). The results of these studies are described here.

EXPERIMENTAL

Materials - Nafion 117 (1100 equivalent weight, proton form) and GT (3.0 μm mean pore diameter) membranes were generously donated by E.I. du Pont de Nemours and W.L. Gore Associates, respectively. Solutions of Nafion were prepared using the procedure of Martin et al. (11). Pyrrole and thiophene were obtained from Aldrich and distilled prior to use. Chromatographic grade PVC was obtained from Polysciences and used as received. Tetraethylammonium tetrafluoroborate was obtained from Aldrich and recrystallized from methanol. Burdick and Johnson acetonitrile was dried over molecular sieves prior to use. Pt foil (0.254 mm thick) was obtained from Aldrich. Other reagents were of highest commercial grades and were used without further purification.

Electrode preparation - 0.5 cm^2 discs were cut from the Pt foil and Cu wires were soldered to one face. These discs were then sealed into 9 mm glass tubes using electron microscopy grade epoxy (Electron Microscopy Sciences). The exposed Pt faces were then polished, sequentially, with 600 grit carborundum, 1.0 μm, 0.3 μm and 0.05 μm alumina on Texmet polishing cloth (all from Buehler). Electrodes were repolished between experiments with the 0.05 μm alumina. A GT membrane was

stretched over the polished face and held in place with a sleeve of heat shrinkable Teflon tubing (10).

The GT membrane was impregnated with Nafion by immersing the membrane-clad electrode into an ethanolic solution of Nafion (2 w/v %) and ultrasonicating for 20 min. The electrode was then removed from the impregnating solution, excess solution was wicked off, and the ethanol was allowed to evaporate for ca. 2 hrs. in air. These electrodes are referred to as Pt/NIGT electrodes. Pt/PVCIGT electrodes were prepared using the same procedure only the Nafion solution was replaced with a 0.25 w/v % PVC solution in tetrahydrofuran.

Nafion film-modified electrodes were prepared by depositing 20 µL of a 4 w/v % Nafion solution (in 50/50 ethanol/water) onto the Pt disc electrode and allowing the solvent to evaporate. Film thickness was estimated assuming a density of 1.58 gm cm^{-3} (12). To study electropolymerization in as-received Nafion membranes, electrical contact must be made with the free-standing membrane (13). This was accomplished by depositing a 50 nm Pt film on one face of a Nafion disc (area = 0.5 cm^2) using a Technics Hummer argon plasma depositor. A Cu wire was attached to the Pt film with silver epoxy and the resulting assembly was embedded into a 9 mm glass tube as described above.

Polymerization and polymer electrochemistry - Electrochemical polymerizations and measurements were accomplished using a Bioanalytical Systems Inc. CV-27 voltammograph in conjunction with a Houston Instruments 2000 X-Y recorder and a Perkin-Elmer strip chart recorder. An aqueous saturated calomel reference electrode (SCE), a Pt flag counter electrode and a single compartment electrochemical cell were used.

Polymerization solutions were 0.74 M in pyrrole or 0.37 M in thiophene, and 0.1 M in tetraethylammonium tetrafluoroborate (Et$_4$NBF$_4$); acetonitrile was the solvent. To insure that the solvent and monomer had permeated the NIGT, PVCIGT and bulk Nafion membranes, the membrane-coated electrodes were ultrasonicated

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briefly in supporting electrolyte and then equilibrated with the monomer solutions for 30 min. prior to electrochemical polymerization. Pyrrole was polymerized as per Diaz et al. by stepping the potential of the Pt electrode to +0.80 V vs. SCE (at the foot of the pyrrole oxidation wave) (8). In some experiments pyrrole was polymerized by scanning the electrode potential through the oxidation wave (e.g., Figure 1). Thiophene was polymerized by stepping the potential to +1.90 V or by scanning through the thiophene wave.

The NIGT membranes were 25 μm thick; the thicknesses of the PP films produced within these membranes were estimated by monitoring the charge consumed during polymerization and assuming that 24 mC cm^{-2} yielded a 0.1 μm film (14). While this is a crude assumption, it is of interest to note that according to this approximation, 6 C cm^{-2} of charge should be required to grow PP completely through the GT membrane and this is precisely what is observed experimentally. Pt/NIGT electodes which have been impregnated with PP or polythiophene (PT) are referred to as Pt/NIGT/PP and Pt/NIGT/PT electrodes, respectively. Note, however, that the PP or PT grows from the Pt-NIGT interface towards the NIGT-solution interface. After polymerization, all membranes and films were extracted in dry, degassed acetonitrile for 30 min. to remove unreacted monomer.

Conductivity measurements and scanning electron microscopy - Electrical conductivity was measured using a conventional four-point conductivity meter (15), constructed in-house. Before the conductivity measurements were made, the membranes were removed from the electrode surface, Soxhlet extracted in acetonitrile for 4 hrs. and then dried in vacuo for 30 min. at ambient temperature. Scanning electron micrographs were obtained on a JEOL JSM-25SII at an accelerating voltage of 25 kV.

RESULTS AND DISCUSSION

<u>Electropolymerization at polymer-coated electrodes</u> - Pyrrole voltammograms at
Pt/NIGT (Figure 1 curve A) are qualitatively similar to pyrrole voltammograms at
bare Pt (Figure 1 curve B). Note, however, that the voltammetric wave at Pt/NIGT
is shifted negatively by ca. 100 mV. The origins of this negative shift will be
discussed in detail below.

With continued scanning into the pyrrole oxidation wave, PP grows into the
NIGT membrane as evidenced by an increase in the capacitive currents (Figure 2),
and the darkening of the, initially white, NIGT. As indicated above,
polymerization may be stopped before the PP film reaches the NIGT-solution
interface; the electode side of such a membrane is black but the solution side is
still white. Alternatively, the PP film may be grown all the way through the NIGT
membrane, in which case both sides of the membrane are black. For a potential step
to +0.80 V, approximately one hour is required for the PP film to grow all the way
through the 25 µm NIGT membrane.

The electrochemical characteristics of Pt electrodes covered with GT membranes
(i.e., no Nafion or PVC impregnation) were also studied. Pyrrole oxidation waves
similar to those shown in Figure 1 are observed at these Pt/GT electrodes
indicating that both electrolyte and pyrrole can permeate the bare GT membrane.
However, PP does not grow through the membrane; instead, PP grows at the Pt-GT
interface and seems to push the GT membrane away from this interface. This
suggests that one of Nafion's roles in the Pt/NIGT system is as an adhesive to
produce strong binding between the NIGT membrane and the electrode surface. Grot
has also suggested that solution-cast Nafion can be used as an adhesive (16).

Electrochemical studies at Pt/PVCIGT corroborate the conclusion that a
membrane/electrode adhesive is required if PP is to be grown <u>through</u> the
membrane. Because PVC is inert and nonionic, it would not be expected to promote
permeation of either the monomer or the polymer through the GT membrane. In fact,

since PVC-impregnation will lower the membrane void volume, PVC should lower the membrane permeability. While the rate of polymerization is lower at Pt/PVCIGT than at Pt/NIGT (see Figure 8 and discussion below) PP grows all the way through the PVCIGT membrane. In analogy to Nafion, solution-cast PVC acts as an electrode/membrane adhesive and thus also allows the PP to grow through the GT membrane.

Finally, it was of interest to see if Nafion could serve as a host material for pyrrole polymerization. In agreement with the results of Fan and Bard, we have found that PP grows through solution-cast Nafion films on Pt electrode surfaces (17). In contrast, pyrrole electrochemistry is not observed at electrodes covered with bulk, as-received Nafion membranes and no PP can be detected, either at the Pt surface or in the Nafion membrane, even after polymerization times as long as 12 hours. While the bulk membranes are somewhat thicker than the solution-cast films, the complete absence of pyrrole electrochemistry and PP indicate that the difference in thickness can not account for these disparate results. Rather, these results corroborate Buttry and Anson's conclusion that solution-cast Nafion has a more open, porous structure than as-received Nafion membrane (18).

Figure 3 shows that thiophene is also oxidizied at Pt/NIGT. These voltammetric waves are qualitatively similar to thiophene waves at bare Pt (19). As was the case with PP, PT is deposited within the NIGT membrane as evidenced by the growth of the polymer redox wave (Figure 3) and the darkening of the NIGT.

Scanning electron microscopy - Electron micrographs (EM's) of bare GT (Figure 4a) show a nodal structure with polytetrafluoroethylene fibers forming webs which extend from the nodes. EM's of NIGT (Fgure 4b) show that Nafion films collect in the polytetrafluoroethylene webs; higher magnification EM's show that Nafion also coats the individual fibers which make up the webs. Clearly, at this loading level (10 w/w % Nafion in the GT), only a small fraction of the available void volume is occupied by Nafion. This explains why ionic diffusion is faster in NIGT than in

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Nafion (10) and why PP is readily grown in the NIGT composite.

An EM for a NIGT/PP membrane is shown in Figure 4c. The pyrrole polymerization time was adjusted such that the PP film just reached the membrane-solution interface and the EM is of this interface. While some of the GT nodal stucture can be seen at the surface, this EM indicates that the bulk of the GT void volume is completely filled by PP. This suggests that NIGT/PP should be much less permeable than NIGT; this conclusion is borne out in experiments described below. Note that the EM's shown are of the surfaces of the various membranes; however, that both Nafion and PP are propogated all the way through the membrane is clearly indicated by the fact that both ions and electrons can pass from one surface, through the bulk, and to the other surface of the membrane.

Electrochemistry of Pt/NIGT/PP and Pt/NIGT/PT - Figure 5a shows cyclic voltammograms for a Pt/NIGT/PP electrode which contains a ca. 0.4 μm PP film within the 25 μm NIGT membrane. These voltammograms are essentially identical to voltammograms obtained at thin PP films on Pt electrodes and show cathodic waves for the reduction of $[(pyrrole)_n^+]$ to neutral PP and anodic waves for the corresponding reoxidation process (14). Peak currents are linearly related to scan rate as is expected for a thin film redox couple (inset Figure 5a). Figure 5b shows cyclic voltammograms for a Pt/NIGT/PT electrode. Again, the polymer electrochemistry is similar to the electrochemistry of Pt/PT (20).

The diminution in capacitive currents upon reduction (Figure 5a) indicates that the PP within the NIGT membrane is an electronic conductor when oxidized and an insulator when reduced. An experiment originally described by Diaz, et al. was used to prove this point (14). Because E^o for ferrocene (Fc) is positive of E^o for the reduction of $[(pyrrole)_n^+]$ (the switching potential, ca. -0.22 V), PP should be an electronic conductor in the potential region where Fc is oxidized. In contrast, E^o for nitrobenzene (NB) is negative of the PP switching potential and PP should be an insulator in the potential region where NB is reduced. Thus, Diaz et

al. have shown that Fc is electrochemically active whereas NB is electrochemically silent at Pt/PP (14). Because Pt/NIGT/PP shows identical electrochemistry (Figure 6), the PP within the NIGT membrane also undergoes an electrochemically induced conductor/insulator transition.

It is of interest to note that when Pt/NIGT electrodes are exposed to CH_3CN solutions containig both Fc and NB (as per Figure 6), redox waves for both couples are observed. This is not surprising since NIGT is both wetted by CH_3CN and highly porous. The absence of NB electrochemistry at Pt/NIGT/PP shows, as anticipated from the EM's, that the PP completely fills the pores of the NIGT membrane.

Figure 7a shows $Fc^{+/0}$ voltammograms at Pt/NIGT/PP electrodes for various thicknesses of PP within the NIGT membrane. While the peak currents for the $Fc^{+/0}$ waves increase with PP film thickness, this increase is due to the superposition of a relatively constant faradaic signal on an increasing capacitive background current. This suggests that the area of the PP electrode which is accessible to the solution redox couple remains relatively constant, irrespective of the total PP film thickness. Since this observation has not been previously noted in the literature, we conducted analogous experiments at Pt/PP electrodes; identical results were obtained (Figure 7b). These data indicate that while small, charge-compensating electrolyte ions can access the entire PP film, larger electroactive species can only access a constant outer, fraction of the PP electrode.

Finally, the increase in peak splitting for the $Fc^{+/0}$ wave with PP film thickness (Figure 7) is probably caused by uncompensated film resistance, the effects of which become more pronounced as the total current increases (21).

The effect of the medium on the electrochemistry of pyrrole – As noted in Figure 1, pyrrole oxidation occurs at less positive potentials at Pt/NIGT than at naked Pt (in both cases the supporting electrolyte was 0.1 M Et_4NBF_4 in CH_3CN.)

There are several plausible explanations for this shift. First, it is at least in principle possible that this shift is caused by a junction potential created by the NIGT membrane. If this is the case, chemically similar redox couples might be expected to show similar positive shifts at Pt/NIGT (i.e., similar redox couples should also be influenced by the junction potential). We have found, however, that $E^{o'}$ for Fc (which like pyrrole is oxidized from a neutral aromatic molecule to a cation radical) at Pt/NIGT is identical to Fc's $E^{o'}$ at naked Pt. This observation suggests that the shift observed is not the result of a junction potential.

The second possiblity is that the oxidation of pyrrole is thermodynamically easier in NIGT than in solution. For example, the electrostatic interaction between the Nafion $-SO_3^-$ sites and the cationic center created upon oxidation of pyrrole could cause a negative shift in the pyrrole oxidation wave (22). While we do not have sufficient data to eliminate this possibility, it is of interest to note, again, that Fc oxidation, which also produces a cationic center, occurs at the same potential in NIGT as in CH_3CN solution. Because the electrostatic interaction is apparently not strong enough to produce a shift in the $E^{o'}$ value for $Fc^{+/0}$, it seems unlikely to us that electrostatics could produce the observed pyrrole shift.

Diaz et al. have shown that the rate determining step in the pyrrole polymerization reaction is the coupling of two electrogenerated cation radicals (e.g., dimerization) (23). It is possible that the positive shift in the pyrrole wave results from acceleration of these radical coupling reactions (24). We currently favor this explanation and are studying simple electroinitiated dimerization reactions in Nafion and NIGT to see if dimerization rates are faster in these media.

Whether dynamically or thermodynamically caused, the negative shift in the pyrrole oxidation wave in NIGT should cause current flow, at any potential, during the electropolymerization to be greater at Pt/NIGT than at bare Pt. Curves A,B and

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in Figure 8 show pyrrole oxidation currents at naked Pt, Pt/PVCIGT and Pt/NIGT, respectively, following a potential step from 0.0 to +0.8 V. Currents at Pt/NIGT are, indeed, greater than currents at naked Pt and Pt/PVCIGT. The fact that polymerization is faster at Pt/NIGT than at Pt/PVCIGT suggests that Nafion is responsible for the observed current enhancement. To test this hypothesis, polymerization currents were monitored at Pt/(solution-cast Nafion) electrodes (Figure 8 curve D). Polymerization currents at Pt/(solution-cast Nafion) are also much higher than at Pt or Pt/PVCIGT. These data seem to confirm the conclusion that Nafion is the essential ingrediant in the observed current enhancement.

An alternative explanation for the data in Figure 8 is that the effective area of the growing PP electrode is greater when the PP is grown within the NIGT or Nafion membrane. To test this possibility, identical quantities of PP were grown at Pt and at Pt/NIGT and cyclic voltammograms for Fc were then obtained at both electrodes. If the Pt/NIGT/PP had a larger effective PP electrode area, Fc oxidation currents at this electrode would be greater than at Pt/PP. Figure 9 shows that Fc oxidation currents are, in fact, slightly larger at Pt/PP than at Pt/NIGT/PP. These data show that the enhanced current at Pt/NIGT (Figure 8) is not an artifact of the electrode area.

Conductivities - NIGT/PP membranes were removed from the Pt electrodes and the electrical conductivities of both the solution sides and the electrode sides of these membranes were measured. The electrode sides showed conductivities which varied between 20 and 50 S cm^{-1}. If polymerization was interrupted before the PP film reached the NIGT-solution interface, the electronic conductivity of the solution face was essentially zero (i.e., the electronic conductivity of NIGT). In contrast, when PP was grown all the way through the NIGT membrane, the conductivity of the solution face varied from 20 to 50 S cm^{-1}. These conductivities compare favorably with conductivities for homogeneous PP films which vary from 10 to 100 S cm^{-1} (25).

CONCLUSIONS

We have shown that electronically conductive composite membranes can be prepared by electropolymerizing pyrrole within Nafion-impregnated Gore-tex. The electronic conductivity of the polypyrrole-doped NIGT membrane is essentially identical to the conductivity of polypyrrole (25). An interesting and potentially useful attribute of these composite membranes is that the conductive element (PP) can be grown to any desired thickness within the host material. Thus membranes which conduct on one surface only but not on the other, membranes which are conductive through out, or even membranes which conduct, independently, on both surfaces but not in the bulk can be prepared.

We have also found that pyrrole oxidation occurs at less positive potentials at Pt/NIGT than at bare Pt. As a result of this negative shift, polymerization currents are higher at Pt/NIGT than at bare Pt. We are currently attempting to ascertain the causes of this shift in oxidation potential. Finally, we have found that Nafion can function as an adhesive to produce strong binding between a membrane and an electrode surface. This could prove to be a useful, general, method for adhering free standing polymer, or other, membranes to electrode surfaces.
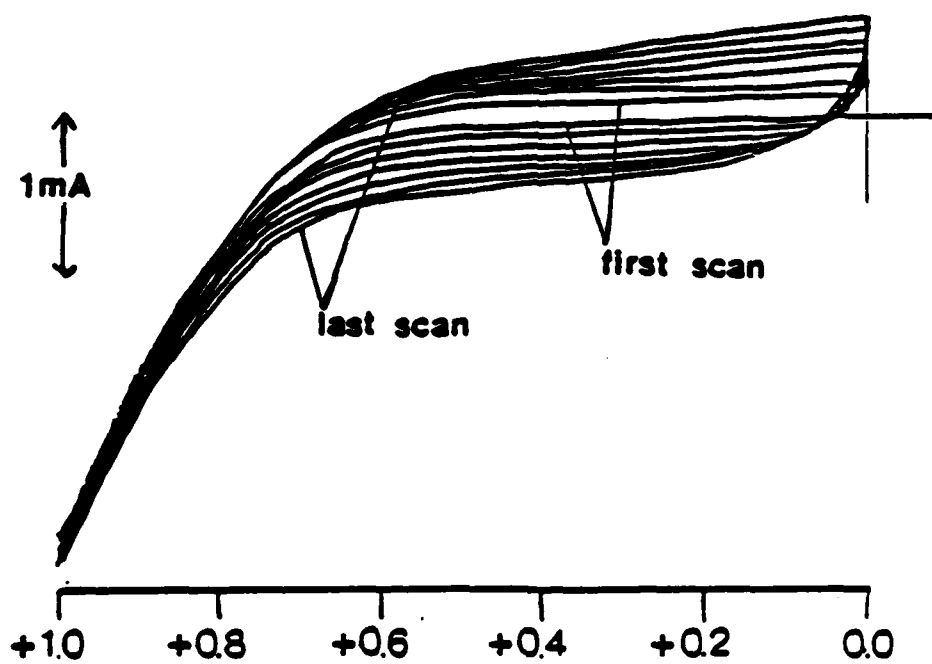
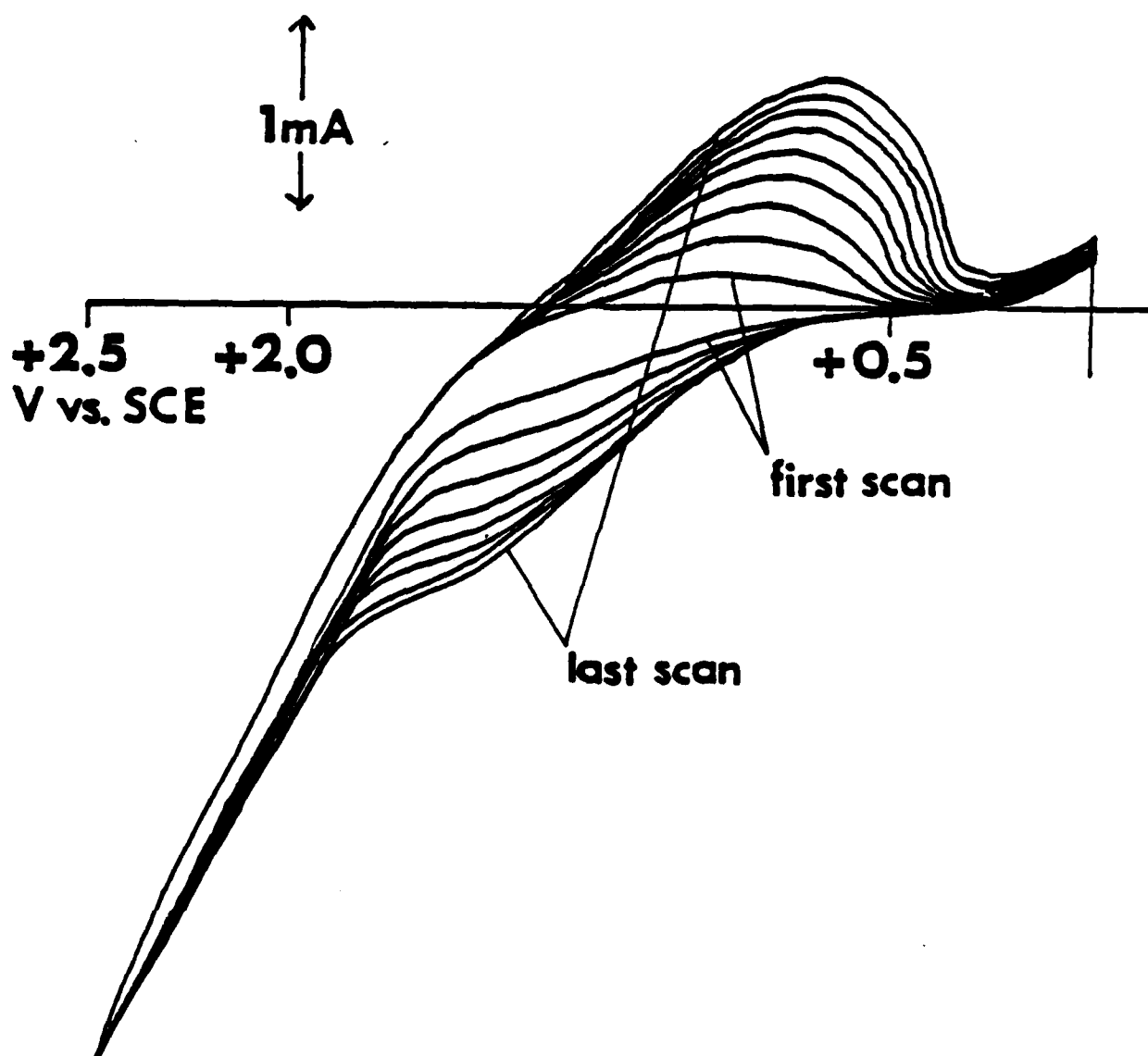## Acknowledgements

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FIGURE CAPTIONS

Figure 1. Cyclic voltammograms (50 mV/s) for 0.74 M pyrrole in 0.1 M Et_4NBF_4, CH_3CN. A. Pt/NIGT electrode. B. Bare Pt electrode.

Figure 2. Cyclic voltammograms (50 mV/s) for pyrrole at Pt/NIGT electrode showing the increase in capacitive currents as a result of PP deposition (solution as per Figure 1).

Figure 3. Cyclic voltammograms (50 mV/s) for 0.37 M thiophene in 0.1 M Et_4NBF_4, CH_3CN at Pt/NIGT.

Figure 4. Electron micrographs for A. Virgin Gore-tex membrane. B. NIGT membrane. C. NIGT/PP membrane.

Figure 5. A. Cyclic voltammograms for PP in Pt/NIGT/PP electrode in 0.1 M Et_4NBF_4. The PP film was ca. 0.4 um thick within 25 um NIGT membrane. Scan rates = 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mV/s (smallest peak currents to largest peak currents, respectively). Inset - Cathodic peak current vs. scan rate for PP waves. B. Cyclic voltammograms for PT in Pt/NIGT/PT electrode (solution as in A). The PT film was ca. 0.2 um thick. Scan rates = 20, 30, 40, 50, 60, 70, 80 mV/s (smallest peak currents to largest peak currents, respectively).

Figure 6. Cyclic voltammetry (20 mV/s) at a Pt/NIGT/PP electrode in a solution 2.6 mM in ferrocene, 12.6 mM in nitrobenzene and 0.1 M in Et_4NBF_4, CH_3CN. The PP film was ca. 0.2 um thick.

Figure 7. Cyclic voltammograms (20 mV/s) for 10 mM ferrocene (0.1 M Et_4NBF_4, CH_3CN). A. At Pt/NIGT/PP electrodes having three different thicknesses of PP within the NIGT membrane. B. At Pt/PP electrodes having two different PP film thicknesses. (The coulomb values associated with the voltammograms in A and B are charges passed during polymerization. For these electrodes, 12 mC = ca. 0.1 um.)

Figure 8. Current during pyrrole polymerization vs. time following a potential step from 0.0 to +0.8 V. A. Pt. B. Pt/PVCIGT. C. Pt/NIGT. D. Pt/(solution-cast Nafion). Solution as per Figure 1.

Figure 9. Plots of anodic peak current for ferrocene oxidation vs. square root of scan rate at A. Pt. B. Pt/NIGT. Solution was 10 mM ferrocene, 0.1 M Et_4NBF_4 in CH_3CN.

+1.0   +0.8   +0.2

V vs. SCE

1.0mA

A
B

1mA

last scan

first scan

+1.0   +0.8   +0.6   +0.4   +0.2   0.0

1mA

+2.5   +2.0   +0.5
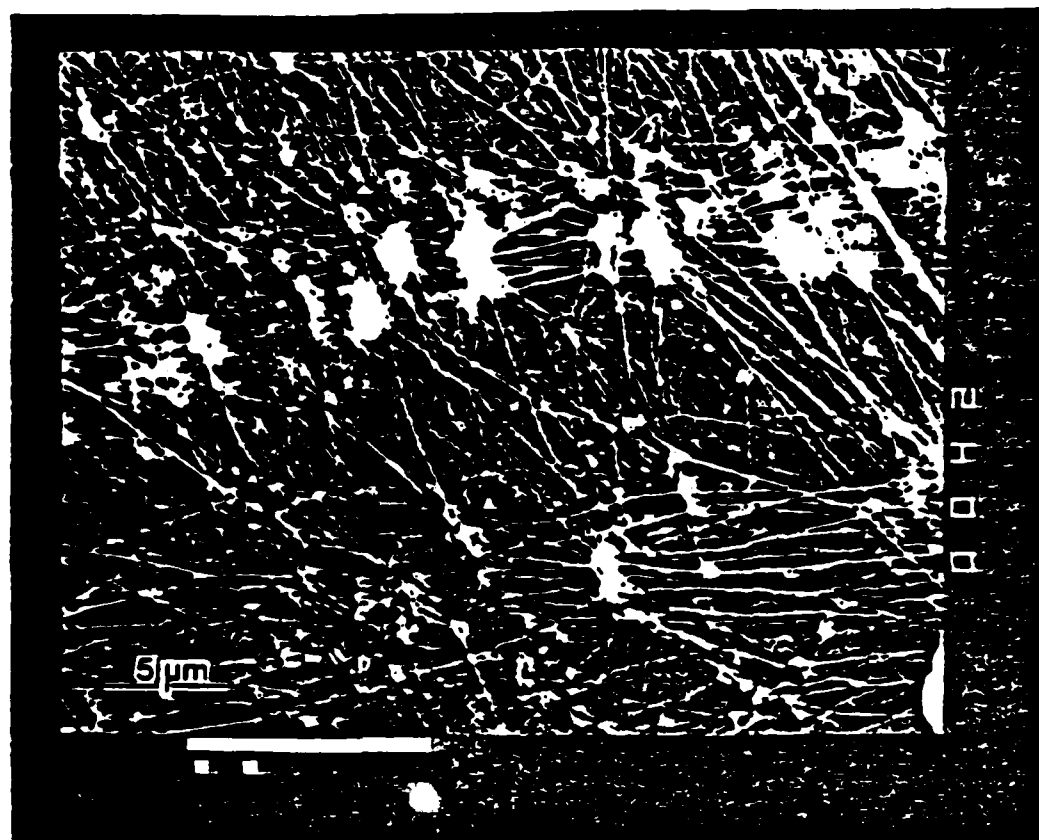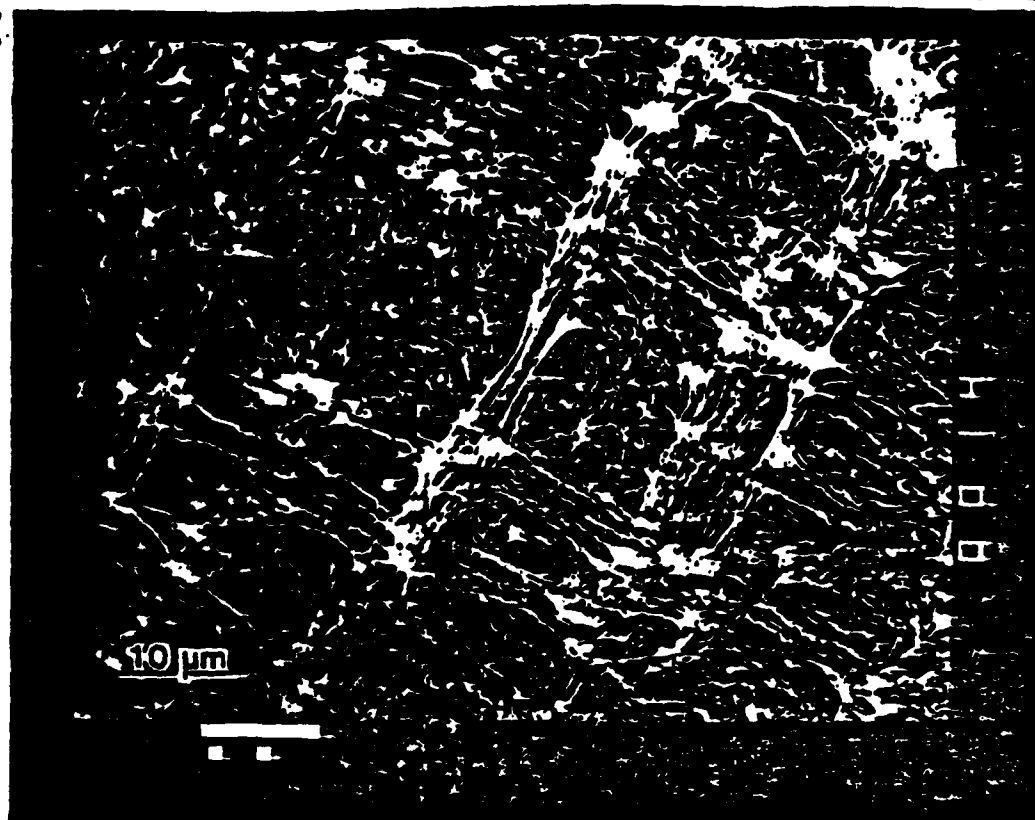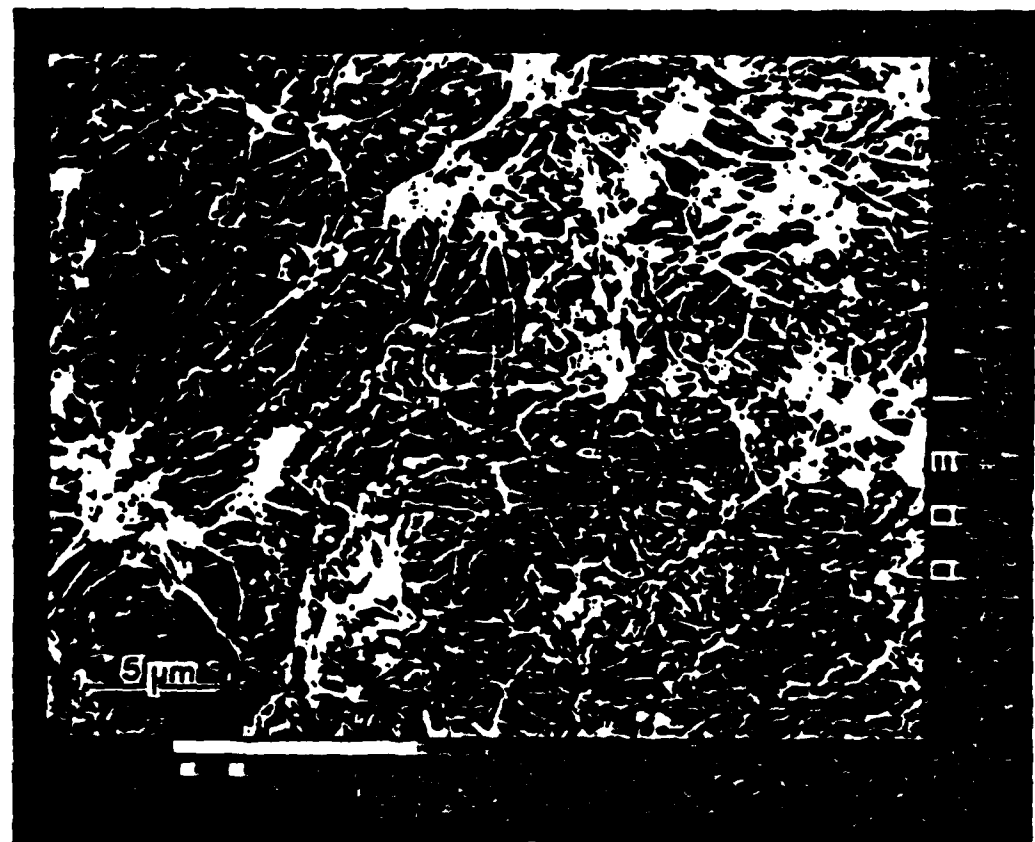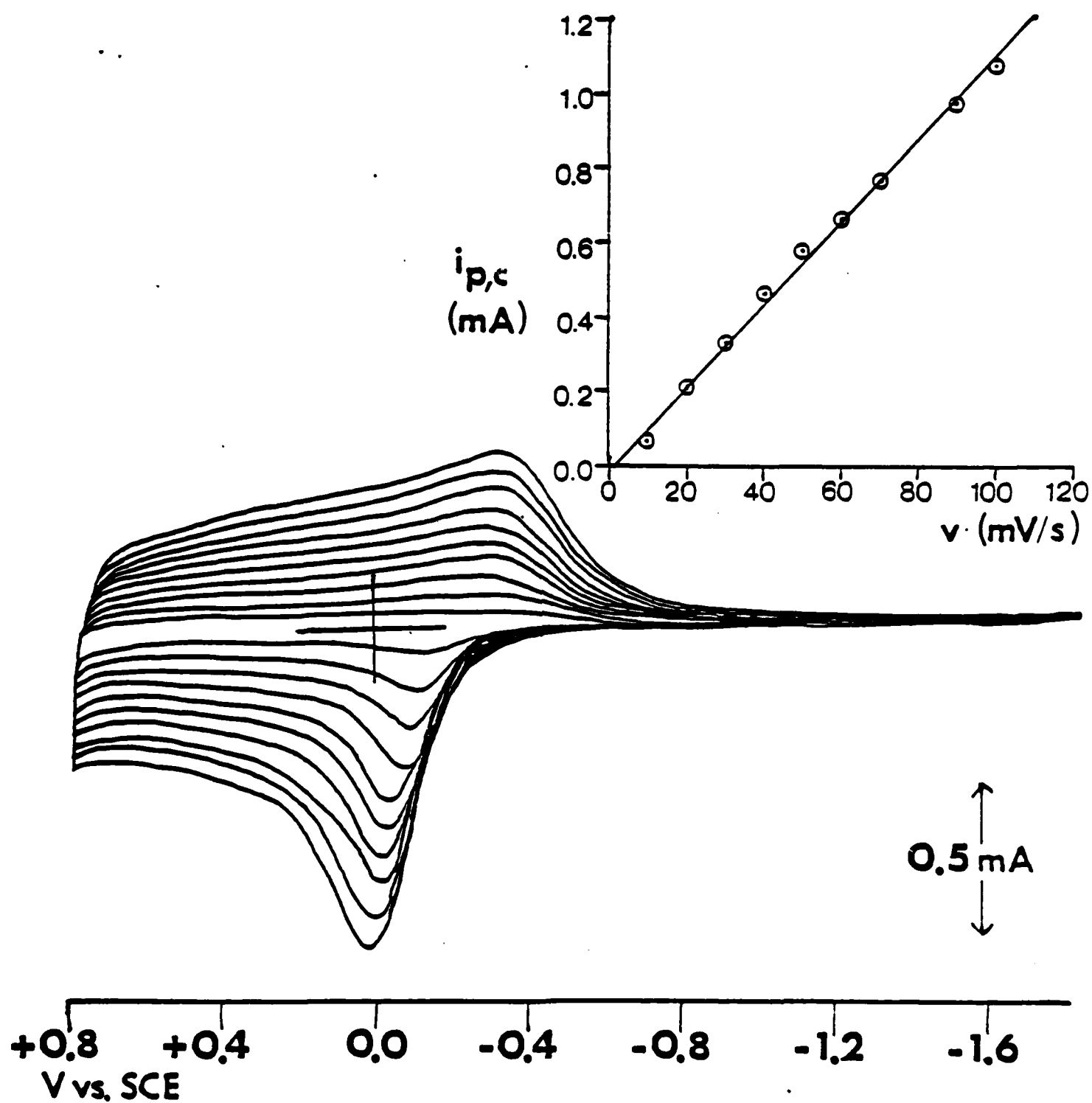V vs. SCE

first scan

last scan
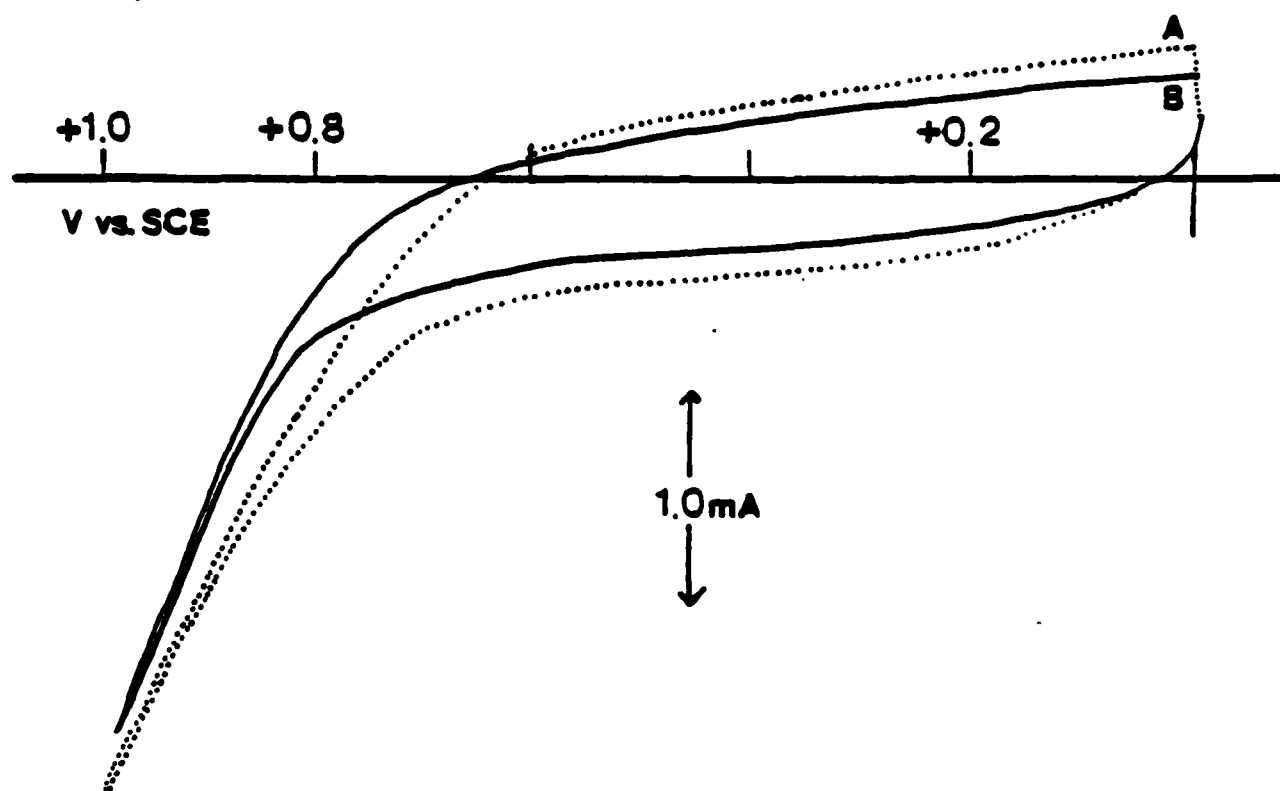
A

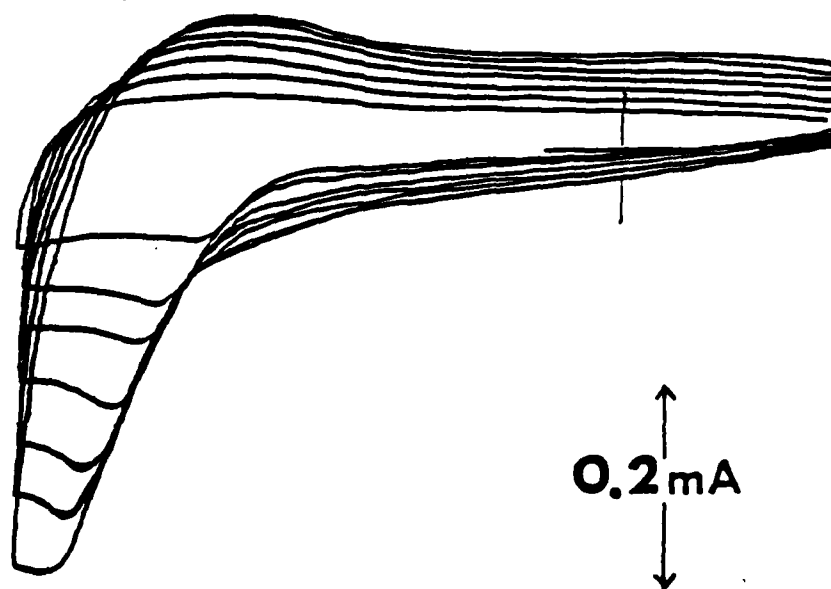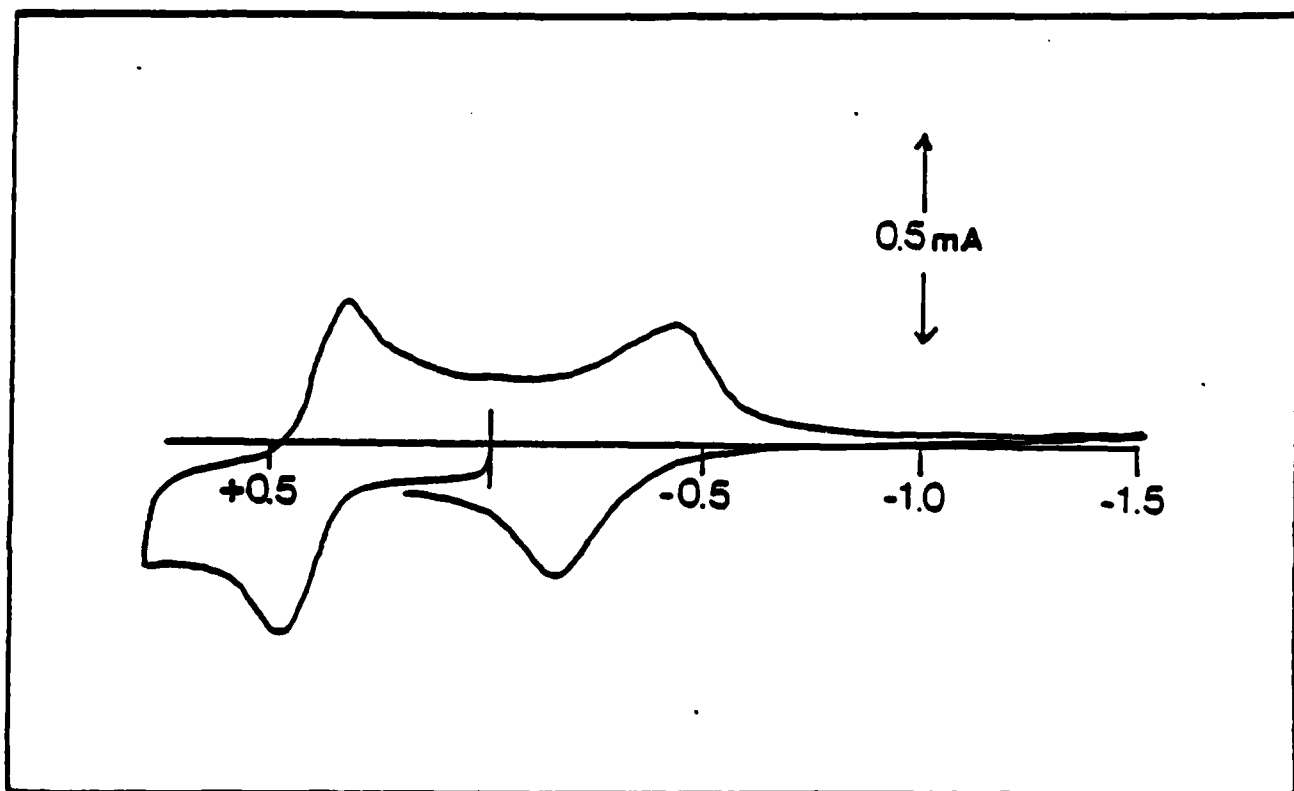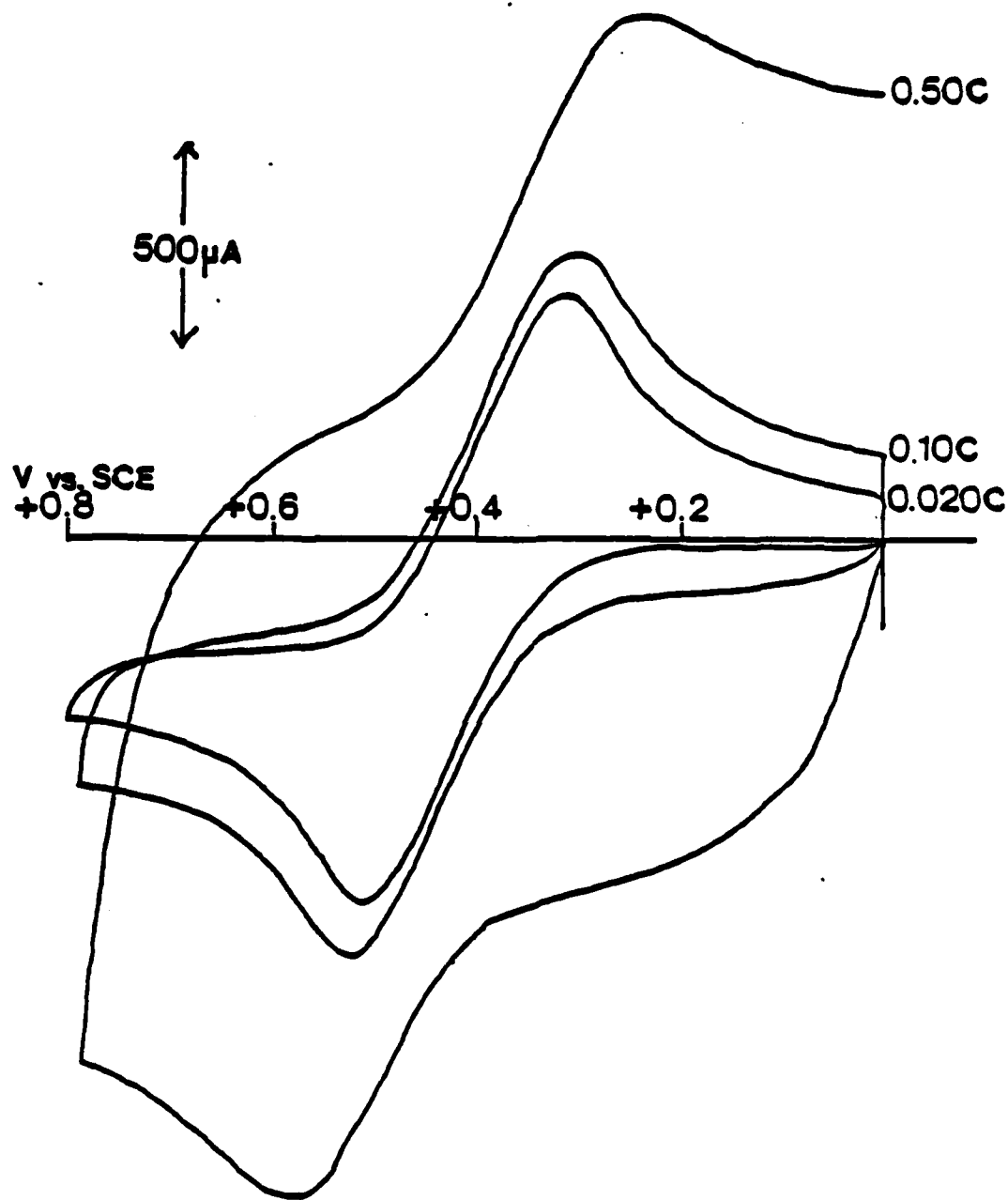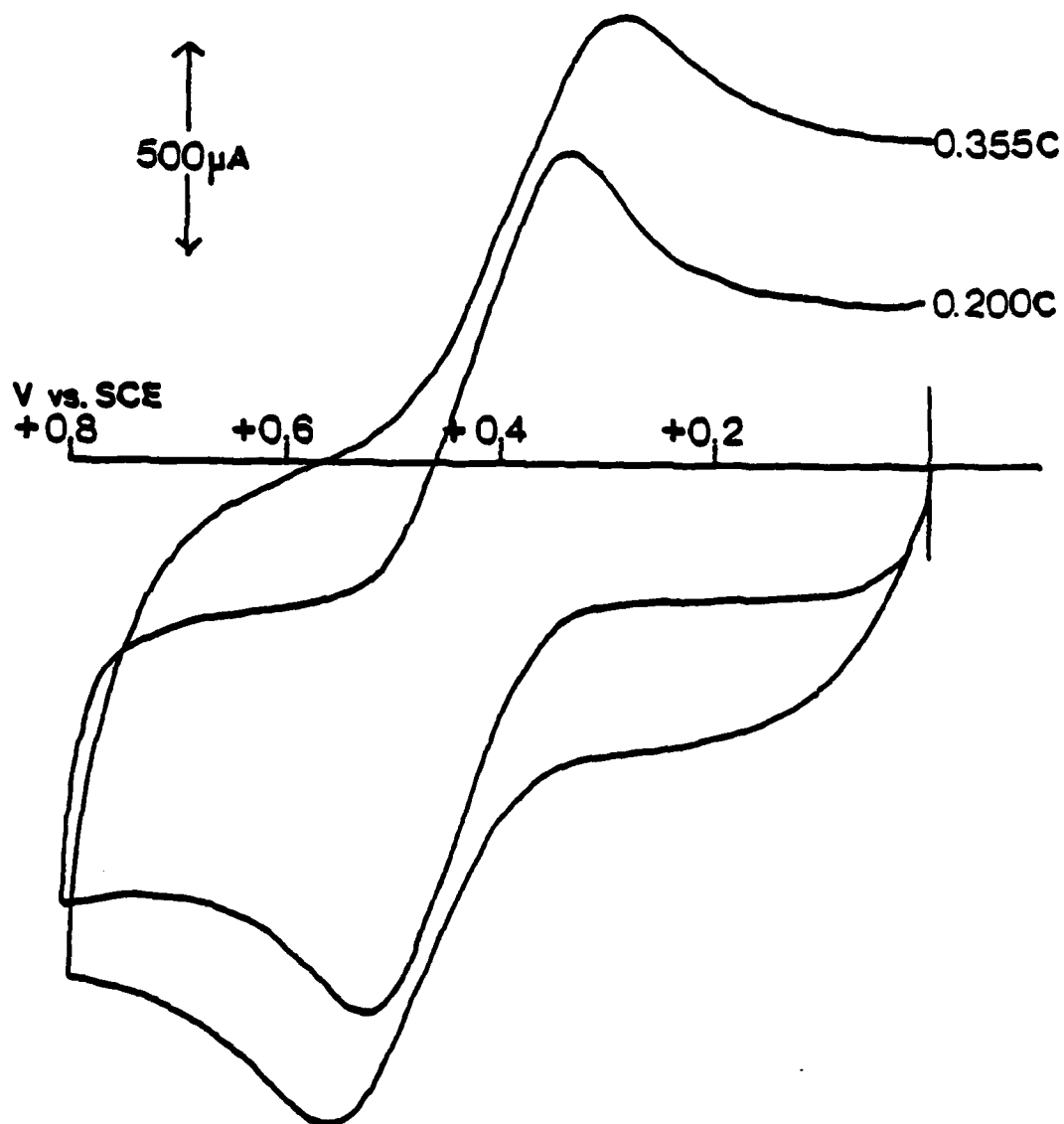Note: You should have original photos for Fig. 4A, B, C (EM's).

CKM

C

10 µm

B

5 µm

Inset plot axes: $i_{p,c}$ (mA) versus v (mV/s)

Main plot axis: V vs. SCE, with marks at +0.8, +0.4, 0.0, -0.4, -0.8, -1.2, -1.6

0.5 mA

0.2 mA

+1.2   +0.8   +0.4   0.0   -0.4

V vs. SCE

END

FILMED

11-85

DTIC